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The NRL CEMAIR Code:

A Disturbed Sea Level Air Chemistry Code

R. F. FRANKLIN

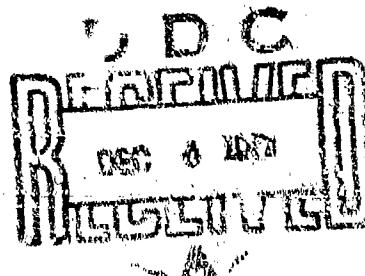
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1. Introduction

When atmospheric air is subjected to either a heating source or an external ionizing source, the chemical, electrical, and thermodynamic properties of the air become altered. Of particular interest are the properties of air plasmas formed by sources such as charged particle beams, beams of electromagnetic radiation, and electrical discharges passing through the air. Such sources can initiate a complicated and diverse set of reactions which radically change the subsequent composition and behavior of the air. A computer code which models in detail the chemical formation and decay of air plasmas would thus be useful for a wide range of applications.

This report describes an air chemistry code, CHMAIR, developed to predict the behavior of air plasmas generated by high power lasers. The code follows the time histories of many particle species and several temperatures under the influence of external heating/ionizing sources. CHMAIR additionally calculates the radiation emitted over a wide band from the disturbed air. The radiation aspect of hot air will be the subject of another report. This report also presents relevant electron impact, excitation and ionization rate coefficients, based on a Maxwellian electron velocity distribution, for the species of interest.

The air chemistry code contains no hydrodynamics; however, it is contemplated that this code or a simpler version of it will be coupled to a hydrodynamics code. A self consistent hydro code with an air chemistry should be of considerable interest in the understanding of air plasmas.

Note: Manuscript submitted August 23, 1979.

2. Disturbed Air Species and Reactions

Pure air at sea level, for our purposes, consists mainly of N_2 and O_2 . When this mixture is subjected to the influence of an ionizing/heating source, positive ions, free electrons, negative ions, atomic species, and molecular species consisting of various combinations of atomic nitrogen and oxygen are formed. Thus, our first generation air chemistry code, CHMAIR, considers the time histories of the following species: N_2 , O_2 , NO , NO_2 , N_2^+ , O_2^+ , NO^+ , N , O , N^+ , O^+ , O^- , O_2^- and e . In addition to those species, the code calculates the time histories of the electron temperature, T_e , the N_2 vibrational temperature, T_v , and the kinetic temperature, T_g , of the heavy particles.

When a volume of air is ionized, the formation and the decay of the plasma are controlled by a large number of atomic, molecular and chemical processes. These processes are indicated below in the details of the reaction kinetics for the species of interest to the current air chemistry code, CHMAIR. However, it should be stated at the outset that several minor atmospheric species, especially CO_2 and H_2O could affect air breakdown and also alter the ensuing air chemistry. These species will be considered in the development of the second generation CHMAIR code.

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm^3/sec))</u>	<u>References</u>
Electron Impact Ionization:		
$e + N_2 \rightarrow e + e + N_2^+$	See Table 1	1
$e + N \rightarrow e + e + N^+$	See Table 1	1
$e + O_2 \rightarrow e + e + O_2^+$	See Table 1	2

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
$e + O \rightarrow e + e + O^+$	See Table 1	1
Electron Impact Dissociative Ionization:		
$e + N_2 \rightarrow N + N^+ + e$	See Fig. 1	3
$e + O_2 \rightarrow O + O^+ + e$	See Fig. 1	3
Radiative Recombination:		
$e + N^+ \rightarrow N + h\nu$	$2 \times 10^{-13} T_e^{-0.5} [1.75 - \log T_e^{0.5}]$	4,5
$e + O^+ \rightarrow O + h\nu$	$2 \times 10^{-13} T_e^{-0.5} [1.75 - \log T_e^{0.5}]$	4,5
Three-Body Recombination:		
$e + e + N^+ \rightarrow e + N$	$8 \times 10^{-27} T_e^{-4.5}$	6
$e + e + O^+ \rightarrow e + O$	$8 \times 10^{-27} T_e^{-4.5}$	6
$e + A^+ + M \rightarrow A + M$	$4 \times 10^{-31} T_e^{-2.5}$	7
Dissociative Recombination:		
$N_2^+ + e \rightarrow N + N$	$4.3 \times 10^{-8} T_e^{-0.39}$	8
$O_2^+ + e \rightarrow O + O$	$1.5 \times 10^{-8} T_e^{-0.7}, T_e \leq 0.1$ $2.1 \times 10^{-8} T_e^{-0.5}, T_e > 0.1$	8
$NO^+ + e \rightarrow N + O$	$2 \times 10^{-8} T_e^{-0.83}$	9
	$9.8 \times 10^{-8} T_e^{-0.37}$	10

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
Charge Exchange:		
$N_2^+ + O_2 \rightarrow N_2 + O_2^+$	$2.7 \times 10^{-12} T_g^{-0.8}$, $T_g \leq 0.3$	11
	$4.2 \times 10^{-11} T_g^{1.4}$, $T_g > 0.3$	
$N_2^+ + N \rightarrow N_2 + N^+$	10^{-12}	12
$N_2^+ + NO \rightarrow N_2 + NO^+$	3.3×10^{-10}	12,13
$N_2^+ + O \rightarrow N_2 + O^+$	$4.2 \times 10^{-12} T_g^{-0.23}$, $T_g \leq 0.13$	14
	$1.6 \times 10^{-11} T_g^{0.41}$, $T_g > 0.13$	
$O_2^+ + NO \rightarrow O_2 + NO^+$	4.4×10^{-10}	15
$N^+ + O \rightarrow N + O^+$	10^{-12}	12
$N^+ + O_2 \rightarrow N + O_2^+$	2.8×10^{-10} , $T_g \leq 0.39$	11,12
	$4.8 \times 10^{-10} T_g^{0.57}$, $T_g > 0.39$	
$N^+ + NO \rightarrow N + NO^+$	8×10^{-10}	12
$O^+ + O_2 \rightarrow O + O_2^+$	$4.6 \times 10^{-12} T_g^{-0.4}$, $T_g \leq 0.155$	11,16
	$10^{-10} T_g^{1.2}$, $T_g > 0.155$	
$O^+ + NO \rightarrow O + NO^+$	7.5×10^{-13} , $T_g \leq 0.1$	17,18
	$3.2 \times 10^{-11} T_g^{1.33}$, $T_g > 0.1$	

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
Ion-Molecule Rearrangement:		
$O^+ + N_2 \rightarrow NO^+ + N$	$3.1 \times 10^{-14} T_g^{-1.0}$, $T_g \leq 0.065$	
	$1.2 \times 10^{-10} T_g^{2.0}$, $0.065 < T_g \leq 0.67$	
	$8.5 \times 10^{-11} T_g^{1.2}$, $0.065 < T_g \leq 0.67$	11, 16
$N_2^+ + O \rightarrow NO^+ + N$	$2.6 \times 10^{-11} T_g^{-0.44} - 4.2 \times 10^{-12} T_g^{-0.23}$, $T_g \leq 0.13$	14
	$1.1 \times 10^{-10} T_g^{0.2} - 1.6 \times 10^{-11} T_g^{0.41}$, $T_g > 0.13$	
$N^+ + O_2 \rightarrow NO^+ + O$	2.8×10^{-10} , $T_g \leq 0.39$	11
	$4.8 \times 10^{-10} T_g^{0.57}$, $T_g > 0.39$	
$O_2^+ + N \rightarrow NO^+ + O$	1.2×10^{-10}	19
Mutual Neutralization:		
$O_2^- + N_2^+ \rightarrow O_2 + N_2$	$2.5 \times 10^{-8} T_g^{-0.5}$	7
$O_2^- + O_2^+ \rightarrow O_2 + O_2$	$6.6 \times 10^{-8} T_g^{-0.5}$	7
$O_2^- + NO^+ \rightarrow O_2 + NO$	$9.5 \times 10^{-8} T_g^{-0.5}$	7
$O^- + NO^+ \rightarrow O + NO$	$7.7 \times 10^{-8} T_g^{-0.5}$	7
$O^- + N^+ \rightarrow O + N$	$4.1 \times 10^{-8} T_g^{-0.5}$	7
$O^- + O_2^+ \rightarrow O + O_2$	$1.6 \times 10^{-8} T_g^{-0.5}$	7

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
$O^- + O^+ \rightarrow O + O$	$4.2 \times 10^{-8} T_g^{-0.5}$	7
$O^- + NO^+ \rightarrow O + NO$	$7.7 \times 10^{-8} T_g^{-0.5}$	7
Dissociative Attachment:		
$e + O_2 \rightarrow O^- + O$	See Fig. 2	20
Attachment:		
$e + O_2 + O_2 \rightarrow O^- + O_2$	$3.5 \times 10^{-31} T_e^{-1} e^{-0.952/T_e}$	21
$e + O_2 + N_2 \rightarrow O^- + N_2$	10^{-31}	21
$e + O \rightarrow O^- + h\nu$	1.3×10^{-15}	21
Associative Detachment:		
$O^- + O \rightarrow O_2 + e$	2×10^{-10}	21
$O^- + N \rightarrow NO + e$	2×10^{-10}	21
Collisional Detachment:		
$O^- + N_2 \rightarrow O_2 + N + e$	$4.8 \times 10^{-10} T_g^{1.5} e^{-0.43/T_g}$	21

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
$O_2^- + O_2 \rightarrow O_2 + O_2 + e$	$1.7 \times 10^{-9} T_g^{0.5} e^{-0.43/T_g}$	21
$O_2^- + O \rightarrow O_2 + O + e$	$3.6 \times 10^{-11} e^{-0.43/T_g}$	21
$O^- + N_2 \rightarrow O + N_2 + e$	$2.3 \times 10^{-9} e^{-2.24/T_g}$	21
$O^- + O_2 \rightarrow O + O_2 + e$	$2.3 \times 10^{-9} e^{-2.24/T_g}$	21

Thermal Dissociation:

$N_2 + N_2 \rightarrow N + N + N_2$	$7.4 \times 10^{-9} T_g^{-0.75} e^{-9.75/T_g}$	22
$N_2 + O_2 \rightarrow N + N + O_2$	$2.2 \times 10^{-9} T_g^{-0.82} e^{-9.75/T_g}$	22
$N_2 + O \rightarrow N + N + O$	$2.2 \times 10^{-9} T_g^{-0.82} e^{-9.75/T_g}$	22
$N_2 + N + N + N + N$	$4 \times 10^{-8} T_g^{-1.5} e^{-9.75/T_g}$	22
$O_2 + N_2 \rightarrow O + O + N_2$	$2.7 \times 10^{-10} T_g^{-1.7} e^{-5.12/T_g}$	22
$O_2 + O_2 \rightarrow O + O + O_2$	$5.8 \times 10^{-9} T_g^{-0.83} e^{-5.12/T_g}$	22
$O_2 + O \rightarrow O + O + O$	$1.3 \times 10^{-8} T_g^{-1.0} e^{-5.12/T_g}$	22
$O_2 + NO \rightarrow O + O + NO$	$1.16 \times 10^{-10} T_g^{-1.8} e^{-5.12/T_g}$	22

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
O ₂ + N + O + O + N	1.16x10 ⁻¹⁰ T _g ^{-1.8} e ^{-5.12/T_g}	22
NO ₂ + M + NO + O + N	1.8x10 ⁻⁸ e ^{-2.84/T_g}	22
NO + N ₂ + N + O + N ₂	1.5x10 ⁻⁹ e ^{-6.5/T_g}	22
NO + O ₂ + N + O + O ₂	1.5x10 ⁻⁹ e ^{-6.5/T_g}	22
NO + N + N + O + N	1.05x10 ⁻⁸ T _g ^{-1.5} e ^{-6.5/T_g}	22
NO + O + N + O + O	1.05x10 ⁻⁸ T _g ^{-1.5} e ^{-6.5/T_g}	22
NO + NO + N + O + NO	1.05x10 ⁻⁸ T _g ^{-1.5} e ^{-6.5/T_g}	22

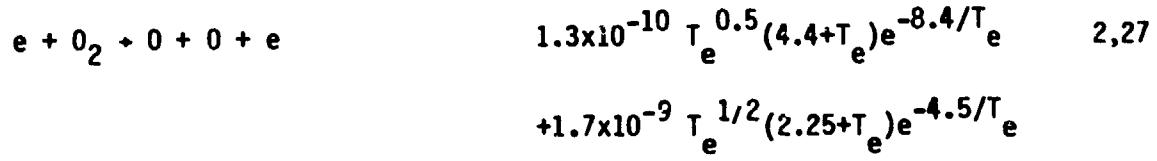
Neutral Rearrangement:

N + O ₂ + NO + O	1.32x10 ⁻¹⁰ T _g e ^{-0.27/T_g}	12
N(² D) + O ₂ + NO + O	4.7x10 ⁻¹¹ T _g ^{0.5}	23,24
O + N ₂ + NO + N	1.3x10 ⁻¹⁰ e ^{-3.27/T_g}	12
N + NO + N ₂ + O	8.2x10 ⁻¹¹ e ^{-0.035/T_g}	12
N(² D) + NO + N ₂ + O	6x10 ⁻¹¹	12

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec))</u>	<u>References</u>
O + NO + N + O ₂	$2.9 \times 10^{-11} T_g^{-1.6/T_g}$	12
N + NO ₂ → NO + NO	6×10^{-12}	25
N + NO ₂ → N ₂ + O ₂	6×10^{-12}	25
N + NO ₂ → N ₂ + O + O	6×10^{-12}	25
O + NO ₂ → NO + O ₂	$1.7 \times 10^{-10} T_g^{-0.52}$	26
NO + NO + O ₂ + NO ₂ + NO ₂	$3.3 \times 10^{-39} e^{0.046/T_g}$	26
Neutral Recombination:		
N + N + N ₂ → N ₂ + N ₂	$6.9 \times 10^{-34} T_g^{-0.75}$	22
N + N + N + N ₂ + N	$3.7 \times 10^{-33} T_g^{-1.5}$	22
O + O + N ₂ → O ₂ + N ₂	$2 \times 10^{-34} T_g^{-0.82}$	22
O + O + O ₂ → O ₂ + O ₂	$8.6 \times 10^{-34} T_g^{-0.33}$	22
O + O + O + O ₂ + O	$1.9 \times 10^{-33} T_g^{-0.5}$	22
O + O + N + O ₂ + N	$1.7 \times 10^{-35} T_g^{-1.3}$	22

<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
$O + O + NO \rightarrow O_2 + NO$	$1.7 \times 10^{-35} T_g^{-1.3}$	22
$N + O + N_2 \rightarrow NO + N_2$	1.1×10^{-32}	22
$N + O + O_2 \rightarrow NO + O_2$	1.1×10^{-32}	22
$N + N + O_2 \rightarrow N_2 + O_2$	$2 \times 10^{-34} T_g^{-0.82}$	22
$N + N + NO \rightarrow N_2 + NO$	$2 \times 10^{-34} T_g^{-0.82}$	22
$N + O + NO \rightarrow NO + NO$	$7.2 \times 10^{-32} T_g^{-1.5}$	22
$N + O + N \rightarrow NO + N$	$7.2 \times 10^{-32} T_g^{-1.5}$	22
$N + O + O \rightarrow NO + O$	$7.2 \times 10^{-32} T_g^{-1.5}$	22
$O + NO + N_2 \rightarrow NO_2 + N_2$	$1.5 \times 10^{-32} e^{+0.05/T_g}$	26
$O + NO + O_2 \rightarrow NO_2 + O_2$	$3 \times 10^{-33} e^{+0.08/T_g}$	26

Electron Impact Dissociation:



<u>Processes Included</u>	<u>Reaction Rate (Coefficient (cm³/sec)</u>	<u>References</u>
$e + N_2 \rightarrow N + N + e$	$6.2 \times 10^{-10} T_e^{0.5} (4.8 + T_e) e^{-9.75/T_e}$	28
Associative Ionization:		
$N + O \rightarrow NO^+ + e$	Detailed balance	2
$N(^2D) + O \rightarrow NO^+ + e$	Detailed balance	2
Photo-Detachment:		
$h\nu + O_2^- \rightarrow O_2 + e$	Wavelength Dependent	29
$h\nu + O^- \rightarrow O + e$	Wavelength Dependent	29

*Note: Three body reaction rate coefficients are in units of cm⁶/sec.

Table I
Electron Impact Ionization Rate Coefficients

Te(eV)	N ₂ Ioniz	N Ioniz	O Ioniz	O ₂ Ioniz
0.2	1.92 (-43)	0.0	3.14 (-38)	2.88 (-38)
0.3	6.14 (-32)	0.0	2.08 (-28)	1.66 (-28)
0.4	3.65 (-26)	0.0	1.71 (-23)	1.32 (-23)
0.5	1.09 (-22)	7.24 (-23)	1.55 (-20)	1.18 (-20)
0.6	2.32 (-20)	3.14 (-20)	1.46 (-18)	1.12 (-18)
0.7	1.08 (-18)	1.61 (-18)	3.81 (-17)	2.96 (-17)
0.8	1.96 (-17)	2.88 (-17)	4.43 (-16)	3.49 (-16)
0.9	1.83 (-16)	2.66 (-16)	3.01 (-15)	2.40 (-15)
1.0	1.15 (-15)	1.57 (-15)	1.40 (-14)	1.12 (-14)
1.1	5.13 (-15)	6.69 (-15)	4.95 (-14)	4.05 (-14)
1.3	5.17 (-14)	6.26 (-14)	3.50 (-13)	2.91 (-13)
1.5	2.86 (-13)	3.25 (-13)	1.49 (-12)	1.25 (-12)
1.7	1.07 (-12)	1.15 (-12)	4.54 (-12)	3.85 (-12)
1.9	3.07 (-12)	3.16 (-12)	1.11 (-11)	9.36 (-12)
2.1	7.25 (-12)	7.2 (-12)	2.29 (-11)	1.94 (-11)
2.3	1.49 (-11)	1.43 (-11)	4.20 (-11)	3.54 (-11)
2.5	2.74 (-11)	2.55 (-11)	7.03 (-11)	5.83 (-11)
2.7	4.62 (-11)	4.20 (-11)	1.09 (-10)	9.00 (-11)
3.0	8.99 (-11)	7.89 (-11)	1.92 (-10)	1.55 (-10)
3.3	1.56 (-11)	1.33 (-10)	3.05 (-10)	2.44 (-10)
3.5	2.15 (-10)	1.8 (-10)	4.00 (-10)	3.14 (-10)
3.8	3.28 (-10)	2.68 (-10)	5.70 (-10)	4.41 (-10)
4.1	4.73 (-10)	3.78 (-10)	7.75 (-10)	5.86 (-10)
4.5	7.21 (-10)	5.60 (-10)	1.10 (-9)	8.10 (-10)
5.0	1.12 (-9)	8.45 (-10)	1.59 (-9)	1.12 (-9)

3. Metastable States

In Section 2 we described the species and the relevant reactions in our multispecies air chemistry code. These species are considered to be in their ground states. However, several metastable states arise in air when it is subjected to an ionization impulse. These are; O(¹D), O(¹S), N(²D), N(²P), N₂(A³ Σ), O₂(a¹A), O₂(b¹E), O⁺(²D), O⁺(²P), N⁺(¹D), and N⁺(¹S). Their influence on emission and deionization processes in the E and F regions of the ionosphere have been considered in detail.^{2, 30, 31} Some of these metastable states have also been considered³¹⁻³³ in multispecies codes for the disturbed D-region.

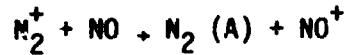
These metastable states store a certain amount of the energy deposited in the disturbed air. Part of this stored energy is released as radiation while the major part is converted into the kinetic energies of the electron gas and the heavy particles. This is due to deexcitation, quenching and charge exchange processes whose rates increase with increasing electron and neutral densities. The emitted radiation from these and short lived states can be utilized, in principle, for diagnostics and tracking of the disturbance. In addition to their influence on the kinetic temperatures, some of the metastables play important roles in the production of new species. Thus, the excitation and deexcitations of the metastable states constitute some of the basic elements of the air chemistry. Detailed excitation and deexcitation mechanisms of these states have been reviewed;^{34,35} in this section we present the important processes and give the relevant reaction rate coefficients utilized in the air chemistry code CHMAIR:

(a) $N_2(A^3\Sigma)$: This state is one of the lowest triplet states of N_2 with a threshold excitation³⁶ energy of 6.2 eV and a lifetime³⁷ of ~ 1 sec. It is excited from the ground state of N_2 by electron impact and by cascade from higher electronic states of N_2 , especially $C^3\pi$ and $B^3\pi$, which are also excited from the ground state by electron impact. The electron impact excitation rate coefficients^{1,3} of the triplet states, $C^3\pi$, $B^3\pi$ and $A^3\Sigma$ are given in Table II as a function of the electron temperature. It should be stated, that the excitation of $C^3\pi$ state is one of the strongest³⁸ for air or pure nitrogen when they are bombarded by high energy electron beams. The $A^3\Sigma$ state is deexcited by electrons through the superelastic collisions and quenched predominantly by O_2 , N , and O with rate coefficients of $2.5 \times 10^{-12} \text{ cm}^3/\text{sec}$ (Ref. 39), $5 \times 10^{-11} \text{ cm}^3/\text{sec}$ (Ref. 40) and $5 \times 10^{-11} \text{ cm}^3/\text{sec}$ (Ref. 41), respectively.

Table II
Electron Impact Excitation Rate Coefficients

T_e	N_2			O_2	
	$A^3 \Sigma$	$B^3 \Sigma$	$C^3 \Sigma$	$a(^1 \Delta)$	$b(^1 \Sigma)$
0.2	1.3(-23)	2.8(-25)	4.7(-33)	5.1(-13)	1.6(-14)
0.3	1.3(-18)	6.8(-20)	8.0(-25)	3.7(-12)	3.2(-13)
0.4	4.3(-16)	3.5(-17)	1.1(-20)	1.2(-11)	1.7(-12)
0.5	1.5(-14)	1.5(-15)	3.2(-18)	2.3(-11)	4.1(-12)
0.6	1.5(-13)	1.9(-14)	1.4(-16)	3.8(-11)	7.9(-12)
0.7	8.3(-13)	1.2(-13)	2.3(-15)	5.5(-11)	1.4(-11)
0.9	8.0(-12)	1.4(-12)	7.9(-14)	1.1(-10)	2.4(-11)
1.0	1.8(-11)	3.4(-12)	2.8(-13)	1.3(-10)	3.2(-11)
1.2	5.9(-11)	1.3(-11)	1.9(-12)	1.9(-10)	4.6(-11)
1.3	9.4(-11)	2.1(-11)	3.8(-12)	2.4(-10)	5.2(-11)
1.5	2.0(-10)	4.9(-11)	1.2(-11)	3.0(-10)	6.7(-11)
1.7	3.4(-10)	9.3(-11)	2.9(-11)	3.5(-10)	7.9(-11)
2.0	4.3(-10)	1.9(-10)	7.8(-11)	4.4(-10)	1.1(-10)
2.5	1.3(-9)	4.4(-10)	2.3(-10)	5.5(-10)	1.3(-10)
3.0	2.1(-9)	7.8(-10)	4.8(-10)	6.5(-10)	1.5(-10)
4.1	3.7(-9)	1.6(-9)	1.2(-9)	7.8(-10)	1.8(-10)
5.0	4.8(-9)	2.4(-9)	1.9(-9)	8.5(-10)	2.0(-10)

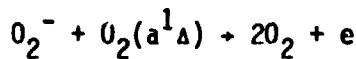
The $A^3 \Sigma$ state can also be excited through the resonant charge transfer



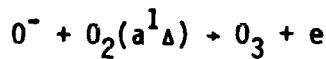
with a rate coefficient of $3 \times 10^{-10} \text{ cm}^3/\text{sec}$.

(b) $O_2(a^1 \Delta)$ and $O_2(b^1 \Sigma)$: These two low lying metastable states of O_2 have excitation³⁶ energies of ~ 1 eV and 1.63 eV, respectively, and lifetimes⁴² of ~ 4000 sec and 12 sec, respectively. They are excited predominantly from the ground state of O_2 by electron impact. The rate coefficients for their excitations^{1,2} are given in Table II. These states are deexcited by superelastic collisions with free electrons. Their quenching by atmospheric species, however, is not fast.³⁴ The effective quencher for $O_2(a^1 \Delta)$ is N and for $O_2(b^1 \Sigma)$ is N_2 .

The corresponding rate coefficients are $3 \times 10^{-15} \text{ cm}^3/\text{sec}$ (Ref. 43) and $2.5 \times 10^{-15} \text{ cm}^3/\text{sec}$ (Ref. 44), respectively. The $a^1\Delta$ also disappears through collisional detachment

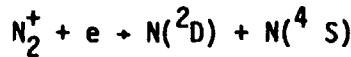


and associative detachment



with rate coefficients⁴⁵ of $2 \times 10^{-10} \text{ cm}^3/\text{sec}$ and $3 \times 10^{-10} \text{ cm}^3/\text{sec}$, respectively.

(c) $N(^2D)$ and $N(^2P)$: These two low lying metastable states of N have excitation energies⁴⁶ of 2.37 eV and 3.56 eV, respectively. Their lifetimes are⁴⁶ $6 \times 10^4 \text{ sec}$ and 13 sec, respectively: They are excited from the ground state of N by electron impact and corresponding excitation^{2,47} rate coefficients are presented in Table III. $N(^2D)$ is excited by the dissociative recombinations



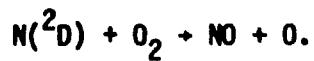
and



where the yield of $N(^2D)$ in the first reaction is near unity⁴⁸ and for the second reaction is⁴⁹ ~ 0.76 .

The low lying states of N can also be excited through electron impact dissociation and dissociative ionization of N_2 . However, no quantitative measurements for the yields exist.

These low lying states are deexcited by superelastic collisions with the free electrons. The most important loss mechanism for $N(^2D)$ is the formation of NO, via



It is also quenched by the atmospheric species N_2 , O and NO with rate coefficients^{34,35} of $1.6 \times 10^{-14} \text{ cm}^3/\text{sec}$, $1.8 \times 10^{-12} \text{ cm}^3/\text{sec}$ and $7 \times 10^{-11} \text{ cm}^3/\text{sec}$, respectively.

Table III
Excitation Rate Coefficients for the Low Lying States of N

T_e (eV)	$^4S - ^2D$	$^4S - ^2P$	$^2D - ^2P$
0.1	8.0(-20)	2.6(-25)	2.10(-14)
0.2	1.54(-14)	2.03(-17)	1.16(-11)
0.3	1.25(-12)	1.11(-14)	9.78(-11)
0.5	4.2(-11)	1.47(-12)	6.0(-10)
0.7	1.98(-10)	1.63(-11)	1.16(-9)
1.0	6.38(-10)	8.91(-11)	2.05(-9)
1.2	1.08(-9)	1.73(-10)	2.56(-9)
1.5	1.52(-9)	3.38(-10)	3.24(-9)
2.0	2.27(-9)	6.54(-10)	4.1(-9)
3.0	3.31(-9)	1.23(-9)	5.18(-9)
5.0	4.50(-9)	1.99(-9)	6.2(-9)

(d) $O(^1D)$ and $O(^1S)$: These two low lying metastable states of O have excitation⁴⁶ energies of 1.96 eV and 4.18 eV, respectively and lifetimes⁴⁶ of 140 sec and 0.3 sec, respectively. They are excited from the ground states of O by electron impact. The corresponding excitation rate coefficients^{2,47} are given in Table IV. They are also excited through the dissociative recombination of O_2^+ . The product results⁵⁰ in 1.0 $O(^3P)$, 0.9 $O(^1D)$ and 0.1 $O(^1S)$, respectively. Furthermore, they can be excited by electron impact dissociation. However, no accurate cross sections for those processes are available. Only approximate rate coefficients² can be obtained using approximate cross sections.²⁷

The deexcitation of these states proceeds through the superelastic collisions with the free electrons. They are quenched by the atmospheric species very effectively at atmospheric densities.

Table IV
Excitation Rate Coefficients for the Low Lying States
of O

T_e (eV)	$^3P - ^1D$	$^3P - ^1S$	$^1D - ^1S$
0.1	1.92 (-18)	1.78 (-28)	2.25 (-19)
0.2	5.28 (-14)	1.96 (-19)	1.76 (-14)
0.3	1.76 (-12)	2.10 (-16)	8.07 (-13)
0.5	3.28 (-11)	6.04 (-14)	1.52 (-11)
0.7	1.21 (-10)	7.25 (-13)	5.4 (-11)
1.0	3.43 (-10)	4.93 (-12)	1.38 (-10)
1.2	5.20 (-10)	1.06 (-11)	1.97 (-10)
1.5	7.94 (-10)	2.32 (-11)	2.76 (-10)
2.0	1.21 (-9)	5.15 (-11)	3.98 (-10)
3.0	1.84 (-9)	1.16 (-10)	5.30 (-10)
5.0	2.52 (-9)	2.21 (-10)	7.16 (-10)

The most effective quenchers of $O(^1D)$ are N_2 , O_2 and NO and their quenching rate coefficients^{34,35} are $5 \times 10^{-11} \text{ cm}^3/\text{sec}$, $7 \times 10^{-11} \text{ cm}^3/\text{sec}$, and $1.7 \times 10^{-10} \text{ cm}^3/\text{sec}$, respectively. For $O(^1S)$, the most effective quencher is $O(^3P)$ where the rate coefficient^{34,35} is $8 \times 10^{-12} \text{ cm}^3/\text{sec}$.

(e) $O^+(^2D)$ and $O^+(^2P)$: These low lying metastable states of O^+ have excitation energies⁴⁶ of 3.32 eV and 5.0 eV and lifetimes⁴⁶ of $\sim 10^4$ sec and 5 sec, respectively. They are excited from the ground states of O^+ by low energy electron impact. The excitation rate coefficients for threshold and near threshold excitation derived⁴⁷ from the relevant collision strengths are given in Table V.

These states also arise as a result of the dissociative ionization of O_2 . However, the only quantitative data on this aspect is given by Stebbings,⁵¹ for incident electron energies from threshold to 100 eV. For 100 eV electrons incident on O_2 the fraction of O^+ excited states, in this case $O^+(^2D)$ and $O^+(^2P)$, could be as high⁵¹ as 0.44. The deexcitation of these states proceeds through the superelastic collisions with the free electrons. However, the most important loss mechanism of $O^+(^2D)$ is the near resonance charge exchange with N_2 and O_2 which may have a rate coefficient as high⁵² as $3 \times 10^{-9} \text{ cm}^3/\text{sec}$. The importance of these reactions is that they convert an atomic ion into a molecular ion which has a larger recombination (dissociative) rate with the free electrons.

(f) $N^+(^1D)$ and $N^+(^1S)$: These low lying metastable states have excitation energies⁴⁶ of 1.89 eV and 4.04 eV and lifetimes of 250 sec and ~ 1 sec, respectively. They are excited from the ground state of N^+ by low energy electron impact. The rate coefficients for these excitations based on threshold collision strengths⁴⁷ are given in Table V. These metastable states, in principle, should arise through the electron impact dissociative ionization of N_2 in a manner similar to the excitation of O^+ metastable states (through the dissociative ionization of O_2 discussed in section 3e).

Table V
Excitation Rate Coefficients for the Low Lying
Metastable States of O⁺ and N⁺ Te in eV.

<u>Transition</u>	<u>Rate Coefficient (cm³/sec)</u>
<u>O⁺</u>	
4S - 2D	$3.2 \times 10^{-8} (T_e)^{-0.5} \exp(-3.33/T_e)$
4S - 2P	$9.5 \times 10^{-9} (T_e)^{-0.5} \exp(-5.0/T_e)$
2D - 2P	$1.4 \times 10^{-8} (T_e)^{-0.5} \exp(-5.0/T_e)$
<u>N⁺</u>	
3P - 1D	$2.7 \times 10^{-8} (T_e)^{-0.5} \exp(-1.89/T_e)$
3P - 1S	$3.5 \times 10^{-9} (T_e)^{-0.5} \exp(-4.04/T_e)$
1D - 1S	$6.5 \times 10^{-9} (T_e)^{-0.5} \exp(-2.15/T_e)$

The deexcitation of these states proceeds through the superelastic collisions with the low energy electrons. Furthermore, the charge exchange process of the metastable states with N₂ are exothermic and should convert an atomic ion into a molecular one. However, no quantitative data exists in this area.

The table referred to in this section gives the excitation rate coefficients as a function of the electron temperature. The corresponding deexcitation rate coefficients can be obtained through the principle of the detailed balance.

Finally, the first generation air chemistry code, CHMAIR, calculates most of these metastable states through steady-state relations. Their effects and their reactions are thus perpetuated accordingly.

4. Inelastic Processes and the Kinetic Temperatures.

Describing the development and decay of an ionized gaseous medium requires a good knowledge of the particle kinetic energies. This is because the ionization and deionization processes depend strongly on these energies. The most accurate method for determining these energies and the resultant ionization is to solve the appropriate Boltzmann equations, coupled to the particle density equations. Such solutions are presently intractable, however, except where numerous simplifications can be made.^{53,54} An alternative approach, used in CHAIR, is to use Maxwellian velocity distributions for the electrons and heavy particles, to express the collision rates as functions of the electron and heavy-particle temperatures. The validity of this assumption has been extensively studied and shown to be not unreasonable for breakdown problems.⁵⁵ The assumption leads to an equation for the electron temperature and an equation for the heavy-particle temperature.

The processes leading to energy losses by electrons in N₂ are ionization, dissociative ionization, dissociation, and excitation of the following electronic states: A³Σ, B³Π, C³Π, E³Σ, a¹Π, two higher electronic groups, and the vibrational excitations of the ground state. The relevant rate coefficients^{1,2,3} for ionization, dissociative ionization, and excitation of the electronic states are given in Tables I-III, VI. The electron impact excitation rate coefficients¹ for the eight ground state vibrational levels, based on measured cross sections,⁵⁶ are given in Table VII.

For N₂⁺, the electronic states considered as energy sinks for electrons, are N₂^{+(B)} and N₂^{+(A)} states. The excitation rate coefficients² for N₂^{+(B)}, excited from the ground state of N₂⁺ based on a measured cross section⁵⁶, are given in Table VI. As for the excitation of N₂^{+(A)} no measured cross section is available; however, an approximate relation based on Seaton⁵⁸ type cross section with a gaunt factor of 0.2 is utilized.

Table VI
Electron Impact Excitation Rate Coefficients

T_e	$E^3 \chi$	$a_{\infty}^{1_N}$	N_2 Opt. Group 2 & 4	$N_2^+(B)$
0.2	2.0 (-35)	7.0 (-31)		1.6 (-14)
0.3	1.1 (-25)	1.6 (-23)		2.4 (-12)
0.5	1.0 (-20)	1.3 (-17)	3.2 (-20) 8.0 (-21)	1.2 (-10)
0.7	1.0 (-16)	5.0 (-15)	4.4 (-17) 1.1 (-17)	7.2 (-10)
1.0	1.7 (-14)	2.5 (-13)	1.0 (-14) 2.5 (-15)	2.0 (-9)
1.2	1.3 (-13)	2.4 (-12)	3.9 (-13) 1.0 (-13)	3.2 (-9)
1.5	9.0 (-13)	1.4 (-11)	8.4 (-13) 2.1 (-13)	5.2 (-9)
2.0	6.2 (-12)	9.9 (-11)	8.0 (-12) 2.0 (-12)	8.3 (-9)
3.0	4.0 (-11)	4.5 (-10)	8.4 (-11) 2.1 (-11)	1.2 (-8)
5.0	1.5 (-10)	1.9 (-9)	7.2 (-10) 1.8 (-10)	1.3 (-8)

Table VII
 $\frac{N_2}{2}$ -Vibrational Excitation Rate Coefficients

T_e/X_v	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
0.1	1.98(-14*)	1.49(-16)	6.28(-17)	1.57(-17)	5.58(-18)	1.37(-18)	2.27(-19)	2.51(-20)
0.2	4.01(-12)	1.48(-12)	8.81(-13)	4.16(-13)	2.16(-13)	1.14(-13)	3.28(-14)	7.81(-15)
0.3	5.63(-11)	2.82(-11)	1.83(-11)	1.05(-11)	6.20(-12)	4.13(-12)	1.45(-12)	6.31(-13)
0.4	2.08(-10)	1.14(-10)	7.59(-11)	4.76(-11)	3.02(-11)	2.24(-11)	6.71(-12)	2.85(-12)
0.5	4.38(-10)	2.52	1.68(-10)	1.11(-10)	7.33(-11)	5.77(-11)	2.39(-11)	8.26(-12)
0.6	6.96(-10)	4.11	2.74	1.88	1.27(-10)	1.04(-10)	4.47	1.60(-11)
0.7	9.43(-10)	5.66	3.77	2.65	1.82	1.52	6.76	2.47
0.8	1.16(-9)	7.04	4.67	3.35	2.32	1.98	9.06(-11)	3.33
0.9	1.34	8.20	5.41	3.96	2.75	2.38	1.10(-10)	4.12
1.0	1.48	9.12	5.99	4.45	3.11	2.72	1.27	4.80
1.1	1.58	9.84(-10)	6.43	4.85	3.38	2.99	1.42	5.37
1.2	1.66	1.04(-9)	6.75	5.15	3.60	3.20	1.53	5.83
1.3	1.71	1.08	6.96	5.39	3.75	3.37	1.62	6.19
1.4	1.74	1.10	7.09	5.56	3.86	3.48	1.69	6.46
1.5	1.76	1.12	7.16	5.67	3.93	3.57	1.74	6.65
1.6	1.77	1.12	7.17	5.75	3.96	3.62	1.77	6.78
1.7	1.76	1.12	7.15	5.79	3.97	3.65	1.79	6.86
1.8	1.75	1.12	7.09	5.81	3.96	3.66	1.80	6.89
1.9	1.73	1.11	7.00	5.80	3.94	3.65	1.80	6.89
2.5	1.56	1.02(-9)	6.26	5.51	3.61	3.45	1.71	6.46
3.0	1.39	9.21(-10)	5.57	5.15	3.36	3.20	1.58	5.88
3.5	1.24	8.29	4.93	4.77	2.93	2.95	1.44	5.29
4.0	1.11(-9)	7.47	4.38	4.43	2.64	2.73	1.32	4.74
4.5	9.95(-10)	6.74	3.90	4.12	2.38	2.55	1.21	4.24
5.0	8.96(-10)	6.11(-10)	3.49(-10)	3.84(-10)	2.16(-10)	2.39(-10)	1.12(-10)	3.80(-11)

*Numbers in parentheses indicate powers of 100 by which the entries are to be multiplied. Where no parentheses are given the entries are multiplied by the power of 10 for the preceding entries.

The inelastic processes through which electrons lose energy in N are ionization and the excitation of the electronic states 2D , 2P , and the optically allowed transitions, especially those with large oscillator strength. The relevant rate coefficients^{1,47} are given in Tables I and III. As for N^+ , the excitations of $N^+(^1D)$, $N^+(^1S)$ and the optically allowed transitions constitute the main inelastic processes for energy loss by electrons. The relevant rate coefficients for 1D and 1S are given in Table V.

The inelastic energy loss processes for electrons in O_2 are ionization, dissociative ionization, and the excitation of the electronic states, a^1A , $b^1\Sigma$, $A^3\Sigma$, and $B^3\Sigma$ where the last two excitations are considered to lead to the dissociation of O_2 . The relevant rate coefficients^{1,2} are given in Section II. As for the excitations of the electronic states of O_2^+ , no relevant experimental cross sections are available, and thus one can only provide estimates for their rate coefficients based on Seaton⁵⁸ type cross sections.

The electron energy loss processes in O considered in CHMAIR are ionization and the excitation of the electronic states 1D , 1S and the optically allowed transitions. The relevant rate coefficients are given in Tables I and IV. As for O^+ , the excitation of 2D and 2P and the optically allowed transitions constitute the main processes for the energy loss by electrons. The relevant rate coefficients are given in Table V.

In addition to the above inelastic processes, the electrons lose their energy also through elastic collisions with the neutrals, Coulomb collisions with the ions, and by Bremsstrahlung radiation. Therefore, the time history of the electron temperature is described in detail, given the source of the original heating, the detailed loss processes discussed in this section, and the corresponding deexcitation processes which heat the low energy electrons.

The air chemistry code calculates two other temperatures, the N_2 vibrational temperature and the heavy particle temperature. The vibrational temperature arises as a result of electron impact collisions with the ground state of the nitrogen molecule where eight vibrational levels are considered to be in a vibrational equilibrium. The electron impact excitation rate coefficients for these levels are given in Table VII, and the corresponding deexcitation rates are obtained through the principle of detailed balance. Several other processes also result in the vibrational excitation of N_2 . One of these is the quenching of $O(^1D)$ by N_2 where⁵⁹ 30% of the internal energy is converted into the vibrational energy of N_2 . The atom-atom interchange forming N_2



also contributes to the vibrational temperature, where one quarter⁶⁰ of the exothermic energy is expended into vibrational energy. The radiative cascade from the $N_2(A^3\Sigma)$ state also raises the vibrational temperature. Processes which result in the loss of vibrational energy are the deexcitation of the vibrational states by electrons through the superelastic collision and quenching by neutral species.

The heavy particle temperature arises as a result of dissociative recombination, electron collisions, charge exchange and neutral rearrangement and quenching processes where some of the exothermic energies are released as kinetic. The dissociative recombinations are an important source of neutral kinetic temperature where the potential energy is converted, partially, to kinetic energy. Other processes affecting the neutral kinetics temperature are the vibrational-translational interchange.

5. Remarks on the Reaction Rate Coefficients

It is obvious from this report that a very large number of reactions occur in an air plasma. Furthermore, almost all of these reactions depend on one temperature or another, which makes the kinetic temperatures of the plasma important elements of the deionization processes in air. However, a large number of these reactions have been measured only at room temperature, or slightly higher. Therefore, the extension of these rates to higher temperatures may be in error. Some reactions have been measured over a wide temperature range and yet with different temperature dependencies. A case in point is the dissociative recombination of NO^+ where one measurement¹⁰ gives a temperature dependence of $T_e^{-0.37}$ while another measurement⁹ gives a temperature dependence of $T_e^{-0.83}$. These two rates are illustrated in Fig. 3 where one recombination rate coefficient is faster than the other by a factor of 3 or more at higher temperatures. Thus the inverse process of associative ionization will clearly be different, depending on which of these dissociative recombination rate coefficients is utilized in conjunction with the equilibrium constant⁶¹

$$K_e = (1.62 T_e + 1.61 T_e^2 + 2.2 T_e^3) \times 10^{-4} \exp(-2.8/T_e)$$

Several processes mentioned in the report have no measured cross sections, for example, the dissociation of O_2 by electron impact. In such cases, the collision rates have been calculated from estimated cross sections,²⁷ which may in themselves be off by an order of magnitude. Other rates are obtained by analogy with similar processes and may not be accurate to better than a factor of 2. However, a good number of important processes have been measured over a wide temperature range, and are reasonably accurate which makes the description of ionization and deionization in air not a hopeless task. Indeed we expect that this air

chemistry code can predict electron densities in reasonable agreement with laboratory measurements (a factor of 2 or better). Finally, many of the electron impact ionization and excitation rate coefficients are given here for a limited electron temperature range for convenience only. Their values at higher temperatures are also available and could be obtained from us upon request.

6. Laser Breakdown as Predicted by CHMAIR

The calculated response of the ambient atmospheric air (300K) to a pulse of CO₂-laser radiation is shown in Figs. 4-6. The laser intensity is 5×10^9 Watt/cm² and is applied for $\tau_p = 0.13$ μ sec. It should be noted that breakdown does not occur for laser intensities below 3×10^9 Watt/cm², in accord with experimental observations⁶²; this breakdown threshold is the intensity at which the loss of electrons due to attachment exactly balances the creation of electrons due to impact ionization.

Figure 4 plots the predicted electron density N_e. The two curves show the different results obtained using two different dissociative recombination rates for the process NO⁺ + e \rightarrow N + O, as measured by Walls and Dunn⁹ and Huang, Biondi, and Johnson¹⁰. Results presented in Figs. 5 and 6 are based on the dissociative recombination rates measured by Biondi and his colleagues.

Figure 5 shows the evolution of the positive ions N₂⁺, O₂⁺, and NO⁺. At late times, the dominant ion is NO⁺, which balances the electron density N_e.

Figure 6 plots N, O, and NO. The reaction N + O \rightarrow NO⁺ + e and its inverse are responsible for the ionization observed at late times.

Finally, this code is being utilized for diagnostic purposes of several air ionization experiments at NRL, and the results will be forthcoming as NRL reports.

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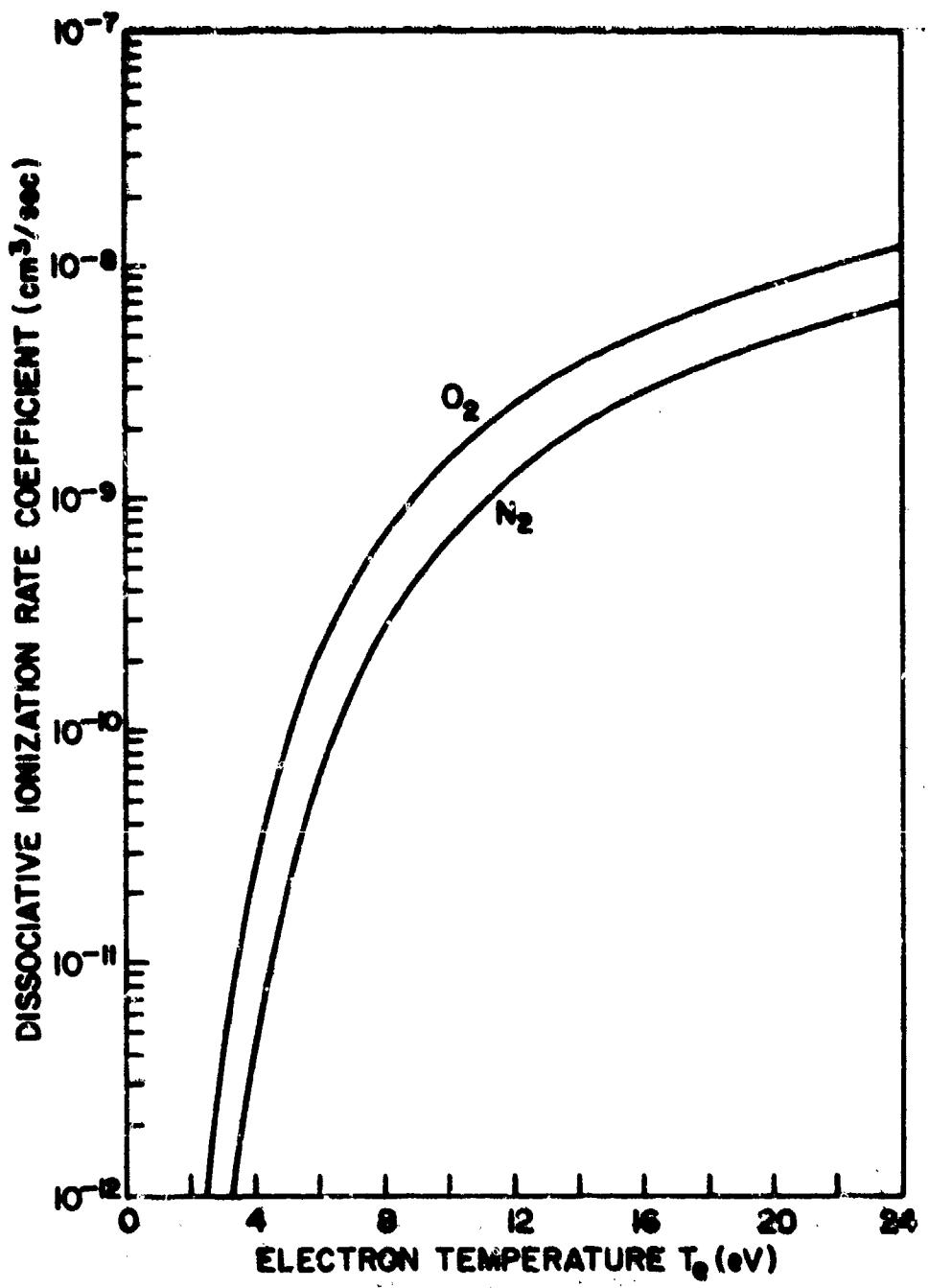


Fig. 1 — Electron impact dissociative ionization rate coefficients of N_2 and O_2 as a function of the electron temperature

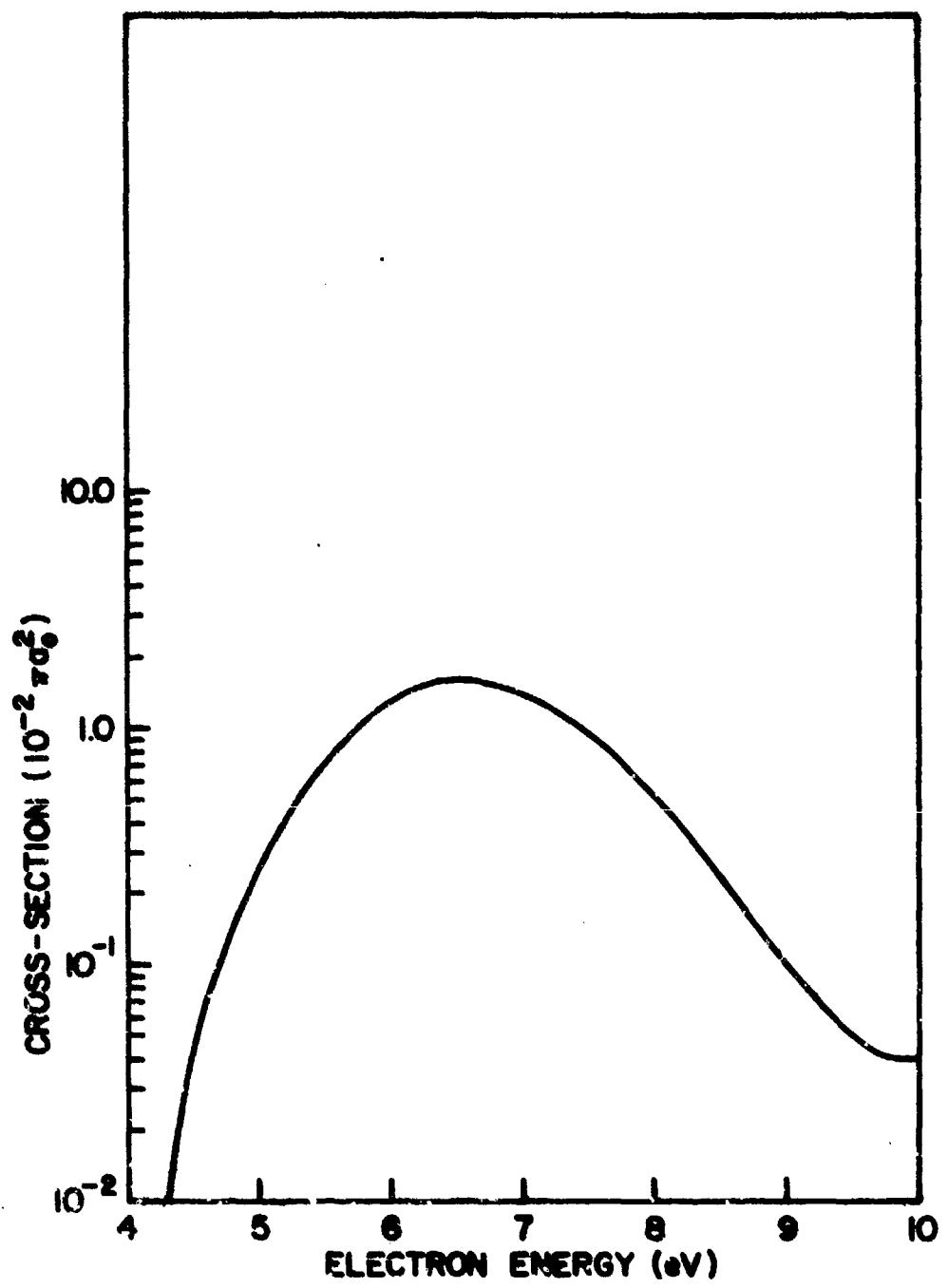


Fig. 2 -- The electron dissociative attachment cross section of O_3

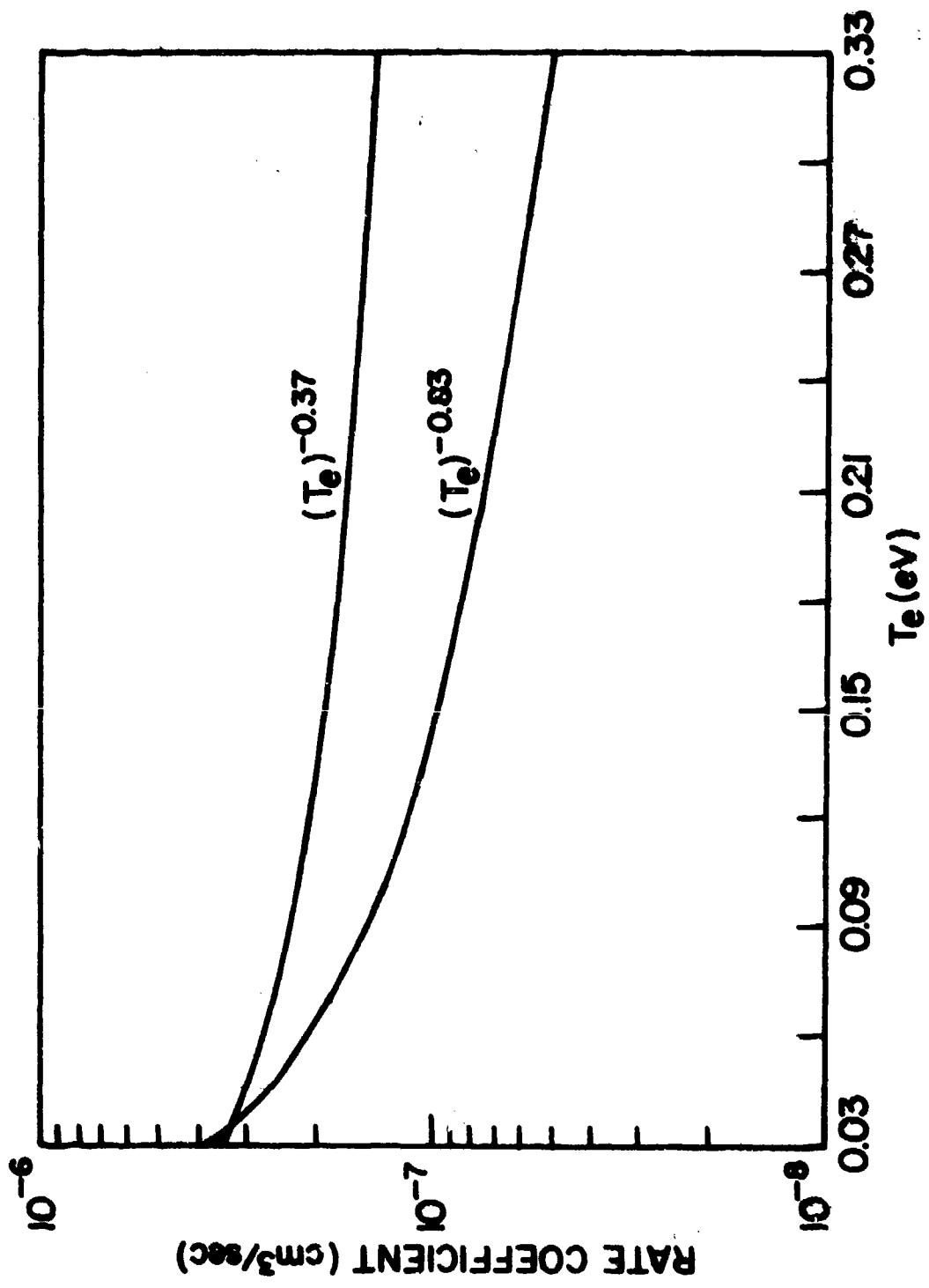


FIG. 8 — Dissociative recombination rate coefficient of NO^+ as a function
 of the electron temperature

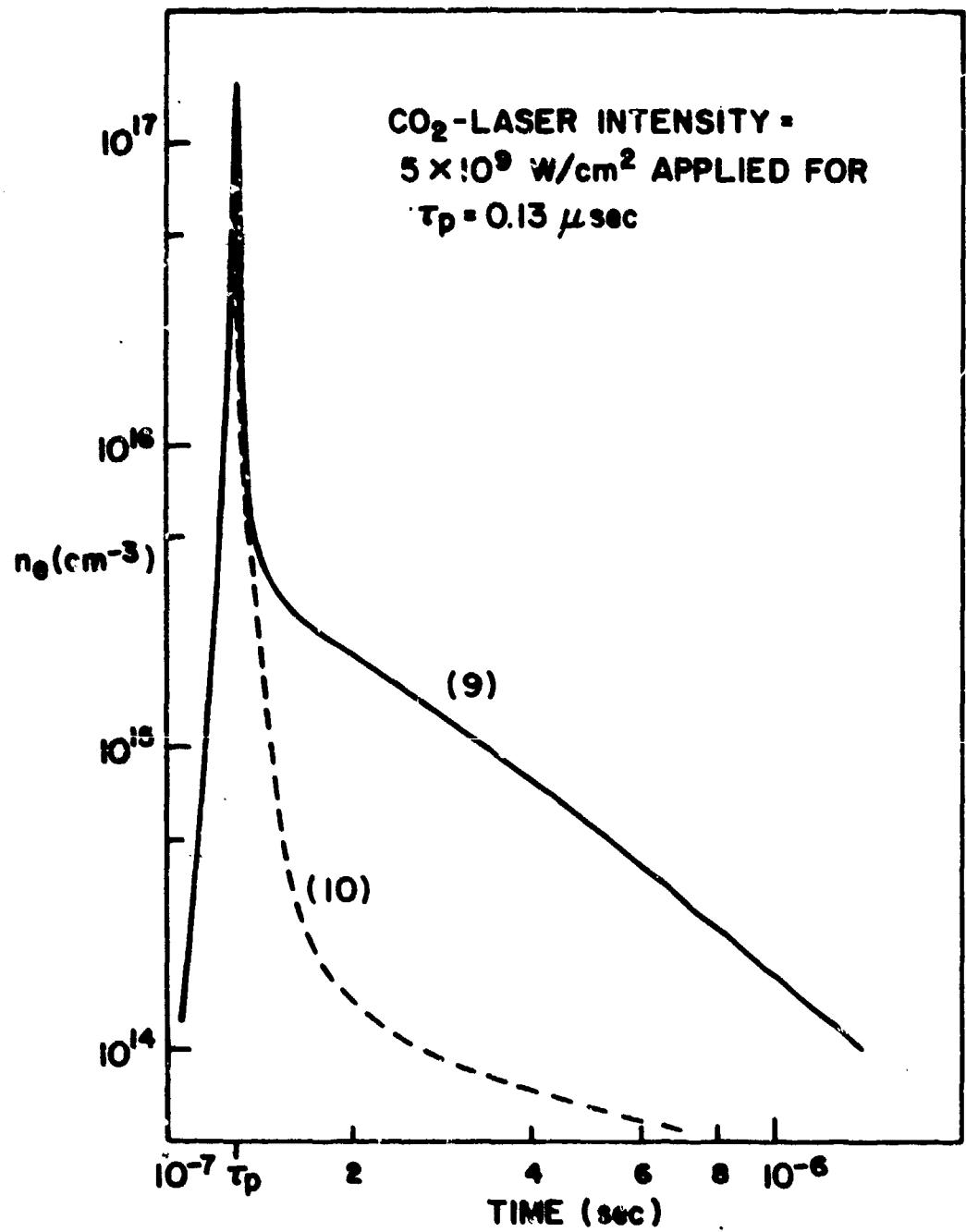


Fig. 4 — The electron density as a function of time for a CO_2 laser produced plasma in air

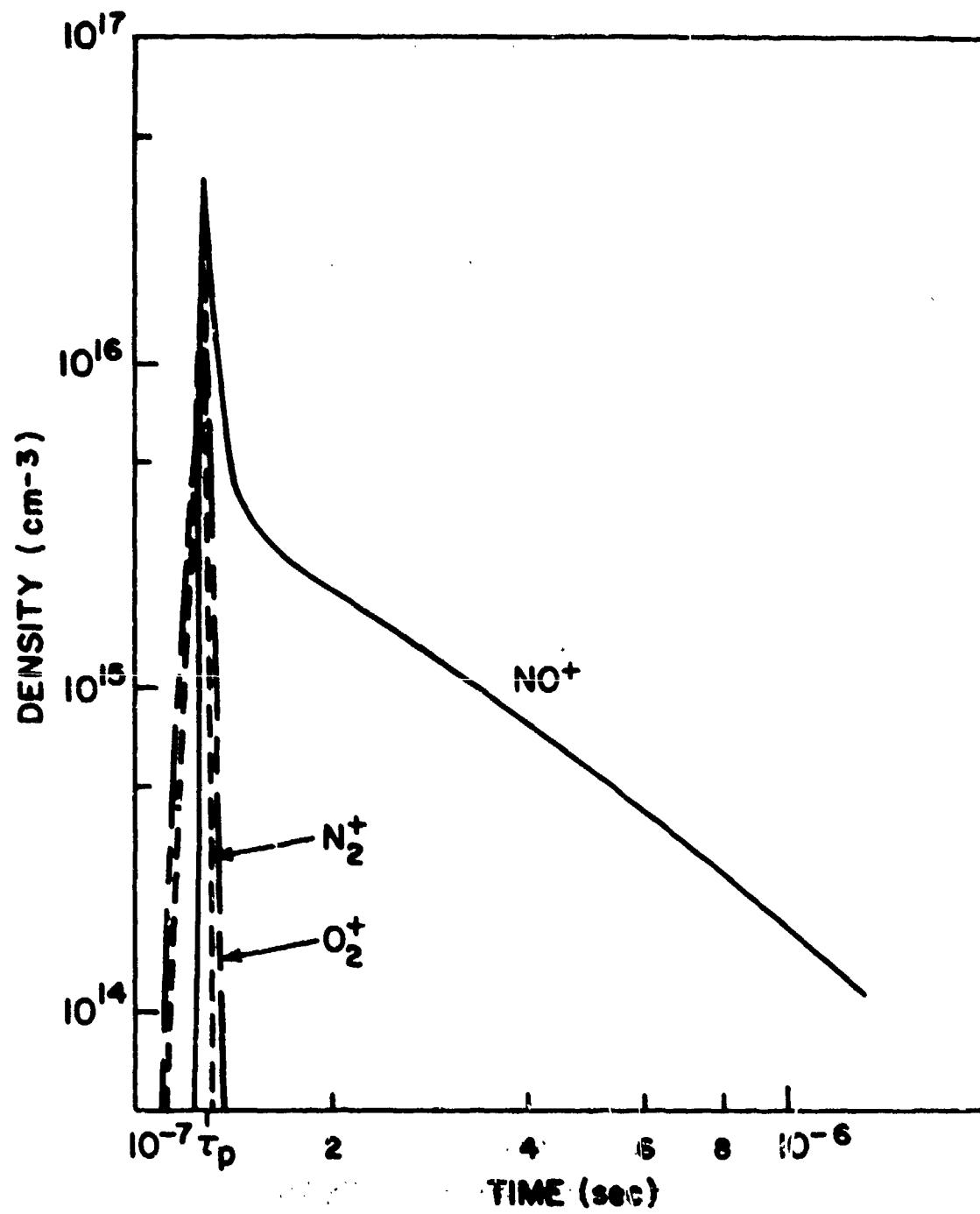


Fig. 5 — The time histories of some air ions for a CO₂ laser produced plasma in air

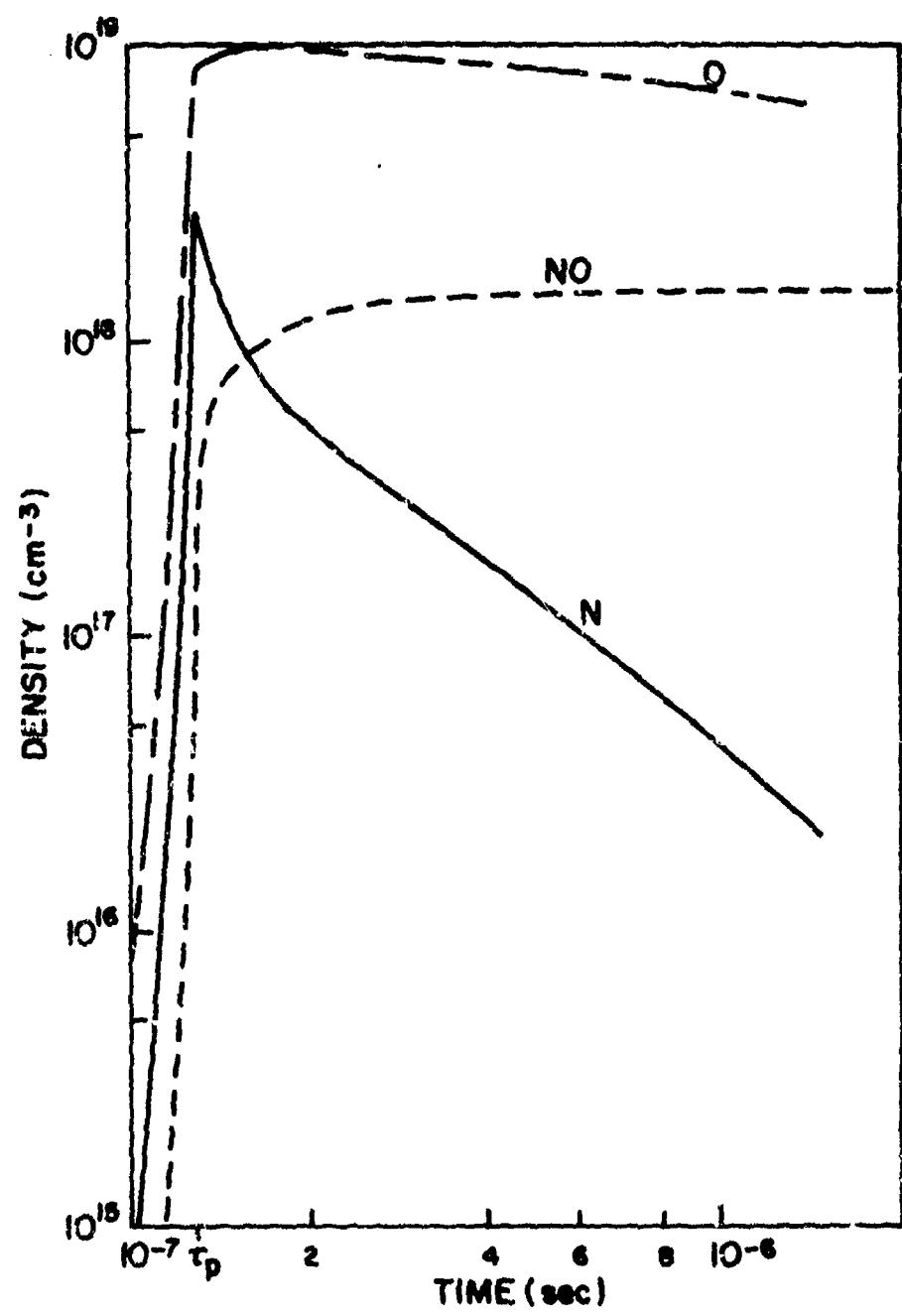


Fig. 6 - The time histories of some neutral species for a CO_2 laser produced plasma in air